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Operational Equations of State.
1. A Novel Equation of State for Hydrocode

by M. A. Grinfeld

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14. ABSTRACT

A novel model equation of state (EOS) for hydrocode is suggested. This model is called the $\Delta\chi$ -EOS because it depends on two functions of one variable each. The $\Delta\chi$ -EOS generalizes the classical incomplete EOS like the ideal gas thermal EOS, the van der Waals EOS, and the virial EOS, among others. We demonstrate the incomplete and complete variants of the $\Delta\chi$ -EOS. We also discuss how to recover the functions Δ and χ from experimental measurements.

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1. Introduction

The equation of state (EOS) is one of the most important notions in thermodynamics. A vast variety of the EOS has been suggested during several centuries of developing thermodynamics. Various applications in dealing with high pressure can be found in references *1* and *2*. During those centuries, the very concept of the EOS itself was significantly changed, modified, and specialized by the greatest minds of physics, engineering, and mathematics. Because thermodynamics is a main interest for various disciplines and communities, different meanings are often assigned to the same terms. In the monograph in reference *3*, the author discusses this semi-linguistic Babel Tower phenomenon regarding the term "chemical potential." Not surprisingly, no full terminological consensus exists between the authors of the valuable reviews (*4–8*). Therefore, in order to avoid possible misinterpretation, we briefly describe our own interpretation of the existing terminology regarding the EOS.

The notion of the EOS appeared well before the discovery of the First Law of Thermodynamics. At that time, the EOS was the function linking pressure P, volume V, and empirical temperature τ – $P = P(V,\tau)$ of a gas or liquid. Today, many researchers call this a thermal EOS.

The discovery of the First Law of Thermodynamics introduced the concept of the internal energy E. This was treated as a function of the volume and empirical temperature $E = E(V,\tau)$ and often called the caloric EOS. Functions $P(V,\tau)$ and $E(V,\tau)$ are deeply connected with each other and cannot be assigned independently of each other. Otherwise, the First Law of Thermodynamics will be violated. Taken separately, none of the functions $P(V,\tau)$ and $E(V,\tau)$ are sufficient for describing all thermodynamic properties of substances.

Later, the discovery and acceptance of the Second Law of Thermodynamics entailed introduction of the absolute temperature T and entropy S. This law reveals an even deeper connection between the functions of thermal and caloric EOS than the First Law did. Moreover, the Second Law suggests treating the internal energy not as the function of the variables (V,τ) but as the function of the pair (V,S): $E = E(V,S)$. The most meticulous theorists call this the complete EOS (see Menikoff [*8*]). Here, "complete" emphasizes that this function taken alone contains as much information as the two functions $P(V,\tau)$ and $E(V,\tau)$ together. At last, when the complete EOS in the form $E = E(V,S)$ is resolved with respect to the entropy, we arrive at the following EOS: $S = S(V,E)$. The last one is coined as the complete EOS for hydrocode. In this very sense, the term complete EOS for hydrocode is used in this report.

The logical foundations of classical thermodynamics remain under much criticism—this is a natural process emphasizing the importance of thermodynamics. Fortunately, this rarely leads to revising the key universal identities valid for complete EOS. Practitioners rarely experience dissatisfaction with the canonical identities for the EOS. However, a variety of novel EOS for novel substances is needed. Because of the technological and engineering advances, even for traditional substances, practitioners demand the extension of the earlier accepted EOS for considerably wider domains of the parameter space. Also, there is an opposite demand of developing various simplified EOS suited for a specific engineering situation.

From a physics and applied mathematics standpoint, the EOS appear to be simple and conceptually transparent in two polar cases. First, the simplicity is achieved in the "big picture" approach of the classical thermodynamics when the most important features only are explicitly taken into account, whereas the variety of minor features deliberately remain unspecified. Second, the simplicity appears in the opposite case of extremely specialized models (e.g., the perfect gas model). Besides being useful in understanding physical phenomena, these cases also allow deep theoretical analysis.

It is now universally accepted that no single EOS can work for all purposes, all substances, and all ranges of thermodynamic parameters. Even if such a universal model were developed, it would only be useful for blind computer implementations and not for further theoretical analysis or intuitive comprehension. Theoretical analysis, however, is very important, even in the computer era.

We suggest a novel model that is rather simple and conceptually transparent. It possesses some features of the big and small pictures previously mentioned. It has infinitely many parametric degrees of freedom. However, the infinitely many degrees of freedom appear not in the form of infinitely many unrelated parameters but in the form of two *functional* degrees of freedom. This model is complete in the thermodynamic sense and includes some classical models as special cases. At the same time, it appears to be convenient for converting the shock-wave locus or the static adiababata locus into the EOS. Explicit formulas of this conversion are given next.

We call our models operational EOS's. The term operational is used because of two reasons. First, the suggested EOS's mostly have the form of various operators with respect to the experimental data used in their definitions. Second, they have direct relation to the Bridgman methodology of operationalism. We will discuss these methodological issues in forthcoming reports after demonstrating several important examples.

2. The Suggested Model

The suggested model is not as general as the most general models of classical thermodynamics. In fact, we suggest a class of the EOS for the hydrocode based on the following two simple constraints:

1. The heat capacity at constant volume C_V is a function of the internal energy density E only:

$$C_V = \chi(E). \tag{1}$$

2. The nondimensional combination PV/RT is a function of the volume V only:

$$\frac{PV}{RT} = \Delta(V), \tag{2}$$

where R is the universal thermodynamic constant.

Some classical EOS's are automatically included in this category. For instance, the model of the monoatomic perfect gas belongs to this category with the following choice of the parametric functions:

$$\chi(E) = \frac{3R}{2},\ \Delta(V) = 1. \tag{3}$$

Another example is the monoatomic van der Waals gas with the vanishing correction coefficient for the internal gas pressure. This classical model corresponds to the following choice of the functions:

$$\chi(E) = \frac{3}{2}R,\ \Delta(V) = \frac{V}{V-b}. \tag{4}$$

In view of what was discussed in the Introduction, even the most innocent-looking assumptions can be thermodynamically inconsistent. In other words, there may not exist any complete EOS for which those assumptions can be deduced in a thermodynamically consistent way. It can be demonstrated, however, that the assumptions 1 and 2 are thermodynamically consistent for any of the two meaningful functions $\chi(E)$ and $\Delta(V)$. Moreover, such a potential can be presented in the following explicit form:

$$S(V,E) - S^* = \int_{V^*}^{V} d\varpi \frac{R\Delta(\varpi)}{\varpi} + \int_{E_*}^{E} \frac{d\xi}{H(\xi)};\ \ H(\xi) \equiv A + \int_{E_*}^{\xi} \frac{d\eta}{\chi(\eta)}\ \ , \tag{5}$$

where A is a constant. The function H has the physical meaning of the absolute temperature.

A simple verification of thermodynamic consistency and validity of equations 1, 2, and 5 is presented in section 2.2.

For the gas model described by equation 4, the EOS implies the following complete EOS for hydrocode:

$$S(V,E) = R \ln \frac{V-b}{V^* - b} + \frac{3R}{2} C_V \ln \frac{E - E_* + C_V A}{C_V A}. \tag{6}$$

2.1 Recovery of the Functions $\chi(E)$ and $\Delta(V)$ From Measurements

The class of substances described by the $\Delta\chi -$EOS is much wider than the classical models. In fact, this class contains two arbitrary functions which can be specified based on the available sets of experimental data.

2.1.1 The Hugoniot Adiabata Data

Given the Hugoniot adiabata locus $E_H(V)$, we get the following Rankine-Hugoniot relationship (*8–10*):

$$2E_H(V) + P\big(V, E_H(V)\big)(V - V_*) - 2E_* + P_*(V - V_*) = 0, \tag{7}$$

which implies the following formula of $\Delta(V)$:

$$\Delta(V) = \frac{2E_H(V) - 2E_* - P_*(V_* - V)}{RH\big(E_H(V)\big)} \frac{V}{V_* - V} \tag{8}$$

and the following complete EOS for hydrocode:

$$S(V,E) = S^* + \int_{E^*}^{E} d\varepsilon \frac{1}{H(\varepsilon)} + \int_{V^*}^{V} d\varpi \frac{2E_H(\varpi) - 2E_* - P_*(V_* - \varpi)}{(V_* - \varpi) H\big(E_H(\varpi)\big)}. \tag{9}$$

In the case of vanishing ambient pressure $P_* = 0$ and when the heat capacity C_V is constant, we arrive at the following simple EOS:

$$S(V,E) = S^* + C_V \ln \frac{E - E_* + C_V T^*}{C_V T^*} + \int_{V^*}^{V} d\varpi \frac{2E_H(\varpi) - 2E_*}{(V_* - \varpi)\left[E_H(\omega) - E_* + C_V T^*\right]}, \tag{10}$$

where T^* is the ambient temperature.

Equations 9 and 10 show that inversion of the experimental measurements of the heat capacity $C_v(E)$ and the Hugoniot locus $E_H(V)$ into the complete EOS for hydrocode $S(V,E)$ is fulfilled with the help of the integral operator. The operator has singularity in the vicinity of the ambient configuration.

2.1.2 The Quasistatic Adiabata Data

The kernel of the integral operator in the recovery formula has a singularity near the ambient state, i.e., for the weak shock waves. Therefore, in the vicinity of the ambient state, some other approaches to recovering the EOS should be used.

The quasistatic adiabata is given by equation $E = E_S^*(V)$. Using equation 5, we get the following inversion:

$$S(V,E) = \int_{E_S^*(V)}^{E} d\xi \frac{1}{T^* + \int_{E_*}^{\xi} \frac{d\eta}{\chi(\eta)}} + S^* . \tag{11}$$

In the case of constant heat capacity at fixed volume, equation 11 reads as follows:

$$S(V,E) - S^* = C_V \ln \frac{E - E_* + C_V T^*}{E_S^*(V) - E_* + C_V T^*} . \tag{12}$$

Equations 11 and 12 show that inversion of the experimental measurements of the heat capacity $C_v(E)$ and the static loading locus $E_S(V)$ into the complete EOS for hydrocode $S(V,E)$ is fulfilled with the help of other operators, as compared with equations 9 or 10. The operators remain integral in the case of nonconstant heat capacity. For the case of constant heat capacity, the operator becomes functional but transcendental. Singularities in this case appear when the ambient absolute temperature is equal to $\mathrm{O\ K}$ as many reserchers prefer. Of course, the assumption of constant heat capacity does not work in the vicinity of $\mathrm{O\,K}$.

For explicit formulas for other types of experimental data, see Grinfeld (*11*).

2.2 Verification of Equations 1 and 2 for the EOS (*5*)

Combining equation 3 with the thermodynamic identities

$$\frac{\partial S(E,V)}{\partial E} = \frac{1}{T}, \quad \frac{\partial S(E,V)}{\partial V} = \frac{P}{T}, \tag{13}$$

we get

$$\frac{P}{T} = R\frac{\Delta(V)}{V}, \qquad T = A + \int_{E_*}^{E} \frac{d\boldsymbol{\eta}}{\boldsymbol{\chi}(\boldsymbol{\eta})} . \tag{14}$$

Thus, the absolute temperature for the model under discussion depends upon the internal energy only, and constant A has the physical meaning of the absolute temperature at $E = E^*$.

Equation 14 proves equation 2. Combining equation 14 with the thermodynamic identity

$$C_V = \left(\frac{\partial T(V,E)}{\partial E} \right)^{-1}, \tag{15}$$

we arrive at equation 2:

$$C_V = \boldsymbol{\chi}(E) = C_V(E) . \tag{16}$$

3. Discussion and Conclusion

We suggest a novel class of simple EOS for hydrocode, depending on two functions of one variable each. The suggested $\Delta\chi-$models generalize some classical models but also allow a wider set of degrees of freedom. Functions $\Delta(V)$ and $\chi(T)$ should be recovered by comparing available experimental data.

This is not the most general form of the complete EOS. Some data, when available, cannot be considered in the suggested framework. A much more general class of the EOS is suggested in a future report (*11*). On the other hand, the suggested model has its own advantages. First, it allows further analytical consideration. Second, it can be recommended in cases where the scope of data is relatively narrow.

We established the explicit formulas for the recovery of the complete EOS for hydrocode from experimental data for the heat capacity at constant volume C_V and the loci of the Hugoniot or static adiabata. The recovery formulas have the form of integral operators with certain singularities. Those formulas can be relatively easily implemented into computer code. Vigilance is necessary in handling the singularities.

The suggested EOS is complete in the sense that it automatically satisfies the First and Second Laws of Thermodynamics.

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